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Formation and Chemical Reactivity of Carbon Fibers Prepared by Defluorination of Graphite Fluoride

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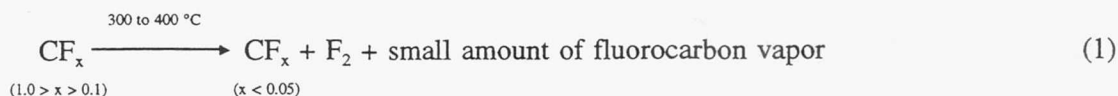
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SUMMARY

Defluorination of graphite fluoride (CF_x) by heating to temperatures of 250 to 450 °C in chemically reactive environments was studied. This is a new and possibly inexpensive process to produce new carbon-based materials. For example, $CF_{0.68}$ fibers, made from P-100¹ carbon fibers, can be defluorinated in $BrH_2C-CH=CH-CH_2Br$ (1,4-dibromo-2-butene) heated to 370 °C, and graphitized to produced fibers with an unusually high modulus and a graphite layer structure that is healed and cross-linked. Conversely, a sulfur-doped, visibly soft carbon fiber was produced by defluorinating $CF_{0.9}$ fibers, made from P-25, in sulfur (S) vapor at 370 °C and then heating to 660 °C in nitrogen (N_2). Furthermore, defluorination of the $CF_{0.68}$ fibers in bromine (Br_2) produced fragile, structurally damaged carbon fibers. Heating these fragile fibers to 1100 °C in N_2 caused further structural damage, whereas heating to 150 °C in bromoform ($CHBr_3$) and then to 1100 °C in N_2 healed the structural defects. The defluorination product of CF_x , tentatively called activated graphite, has the composition and molecular structure of graphite, but is chemically more reactive. Activated graphite is a scavenger of manganese (Mn), and can be intercalated with magnesium (Mg). Also, it can easily collect large amounts of an alloy made from copper (Cu) and type 304 stainless steel to form a composite. Finally, there are indications that activated graphite can wet metals or ceramics, thereby forming stronger composites with them than those the pristine carbon fibers can form.

INTRODUCTION

A previous study at NASA Lewis Research Center showed that, when heated to 300 to 400 °C in an inert environment, graphite fluoride (CF_x) fibers lost most of their fluorine atoms but very little carbon. Such heating produced carbon fibers that contained small amounts of fluorine (5 percent carbon or less) and, according to x-ray diffraction data, had the same molecular structure as pure graphite (ref. 1). This phenomenon, defluorination, is illustrated in the following:



In previous studies, CF_x powder was thought to be stable at temperatures below 400 °C and explosive if heated rapidly at temperatures above 400 °C (ref. 2). Near-complete defluorination in the temperature range of 300 to 400 °C was not observed.

This new discovery suggests that breaking the carbon-fluorine bonds in CF_x is not as difficult as previously thought. Therefore, the following question was raised: In the presence of other reactive chemicals at certain temperatures and pressures, can CF_x be chemically transformed into other carbon-based materials during

¹P-25, P-100, P-125, P-140, and T-300 are product numbers of Amoco Performance Products, Inc., Atlanta, GA.

defluorination? This general question led to more specific questions that, as addressed herein, may lead to the development of many new processes and products. For example,

(1) Can graphite fibers with cross-linked graphite layers and/or crystallites be produced by introducing a "bridge" (i.e., a chemical with more than one functional group) into the CF_x structure (fig. 1) to bond with carbon atoms at different layers and/or crystallites during defluorination?

(2) Can fibers with diamond or diamond-like structures be produced by allowing carbon-containing molecules to enter the CF_x structure and bond to the carbon atoms at different layers during defluorination, while keeping the sp^3 electronic structure for the carbon atoms?

(3) Can C_{60} (a recently discovered form of carbon) be produced by first heating CF_x in a certain environment at a specific temperature to produce a structurally damaged carbon material, and then further heating the damaged carbon to a higher temperature to evaporate it?

It was hoped that this research would reveal the possibility and value of using CF_x as a reactant to develop processes that could produce new carbon-based products.

EXPERIMENTS

Unless otherwise stated, the CF_x reactants used in this research were obtained by exposing the bromine- and iodine-intercalated P-100 fibers to several cycles of 1-atm fluorine (F_2) and 1-atm nitrogen (N_2) at 350 to 370 °C (refs. 1, 3, and 4). All P-100 samples were taken from the same commercially purchased spool.

CF_x was exposed to a number of different chemicals and the fiber products were further heat treated. The fibers' physical and chemical properties before and after heat treatment were measured. Their potential uses will be discussed herein.

Nitrogen

Nitrogen is believed to be chemically inert to CF_x . In this study, the changes resulting from CF_x defluorination in pure N_2 (99.99 vol %) were recorded and compared with the changes resulting from CF_x defluorination in other reactive chemicals. Such comparison reveals the effects of the surrounding reactive chemicals during defluorination.

Weight, x-ray diffraction data, and energy dispersive spectra (EDS) data of the $CF_{0.68}$ samples during 350, 400, or 450 °C heating in N_2 were measured. Subsequent heating of the defluorinated but unexploded samples to 1100 °C in N_2 produced a new carbon material whose physical properties were also examined.

The color and weight of a $CF_{0.9}$ sample (originally gray) made from P-25 fibers were also monitored during a N_2 heating period where the temperature increased from room temperature to 1100 °C.

Air

In a previous study, it was concluded that, in air, the weight of $CF_{0.65}$ samples remained unchanged at 200 °C, but decreased significantly at temperatures higher than 300 °C (ref. 1). In this study, weight, x-ray diffraction data, and EDS data of the $CF_{0.68}$ samples during 350 and 400 °C heating in air were measured. These data were used to study the oxygen- CF_x reaction.

Bromine

CF_{0.65} samples were placed in five different kinds of bromine (Br₂) environments: liquid Br₂ at -7, 14, and 34 °C, and 1-atm Br₂ vapor at 200 and 350 °C. The first three conditions were selected to examine how Br₂ reacts with CF_x at the temperatures used for graphite intercalation with Br₂. The last two conditions were selected to examine how Br₂ reacts with CF_x at temperatures that could weaken or break the carbon-fluorine bonds (see eq. (1)).

Two CF_{0.68} samples were each exposed to 1-atm Br₂ vapor at 350 and 450 °C, respectively. The results of these two runs were compared with the results obtained from the process described in the previous paragraph. This comparison shows that CF_x fibers with different empirical formulas reacted to Br₂ differently.

Unless otherwise stated, CF_{0.68} fibers were used for the rest of this research.

Sulfur

Several CF_{0.68} samples were exposed to sulfur (S) vapors at temperatures ranging from 300 to 450 °C. Some fibers were pretreated with S at 230 to 260 °C to pick up as much S as possible before defluorination. Preliminary experiments showed that, at 260 °C or lower in S, the CF_x fibers can absorb some S but only lose a small amount of fluorine. This experiment was done to determine if S could use its several bonds to cross-link carbon atoms and/or heal the structural defects in the fibers during defluorination.

Several kinds of CF_x materials were also used to examine the CF_x-S chemical reaction to determine if different CF_x materials react differently to produce unique products. Materials include commercially obtained CF_{0.9} powder, CF_{0.9} obtained by fluorinating P-25 fibers, and a polytetrafluoroethylene (PTFE) sample.

Carbon tetrachloride, Bromoform, Acetylene tetrabromide, and 1,4-diabromo-2-butene

The CF_{0.68} samples were placed in liquid forms of carbon tetrachloride (CCl₄), bromoform (CHBr₃), acetylene tetrabromide (C₂H₂Br₄), and 1,4-diabromo-2-butene (BrH₂C-CH=CH-CH₂Br) for a period of 20 hr to 4 days. The fibers were then heated to between 350 and 450 °C so that they reacted to the chemicals at 1-atm pressure when the carbon-fluorine bonds were about to break (see eq. (1)). Again, this experiment was conducted to study whether the carbon in these organic chemicals can be used to heal the defects resulting from defluorination or to perform cross-linking for carbon atoms in the fibers, resulting in new carbon structures.

A sample of CF_{0.9}, obtained by fluorinating P-25, was defluorinated in C₂H₂Br₄, again to determine if different kinds of CF₂ materials have different chemical reactivities and produce different products.

Tin and lead

The CF_{0.68} samples were placed between two thin layers of solder (tin-lead mixture) or two thin layers of lead. Both three-layer samples were placed between two graphite blocks which were then tightly wrapped with T-300 carbon fibers. The complete systems were placed in N₂ at 450 °C. This experiment was designed to determine if tin (Sn) and lead (Pb) would react with CF_x when the carbon-fluorine bonds broke (see eq. (1)), resulting in a molecular structure similar to that of SiC.

Heat Treatment

Most of the fiber products just described were heated to 600 or 1100 °C in N₂. Three of the products heated to 1100 °C (CF_{0.68} made from P-100 and defluorinated in S, Br₂HCCHBr₂, and BrH₂CCHCHCH₂Br environments, respectively), along with pristine P-100 and P-25 samples, were subsequently heated to 2700 °C for 40 min in argon (Ar). In this process, the temperature was first kept at 1100 °C for 20 min before raising to 2700 °C in 1 hr.

Thermal Stability of Heat-Treated Fibers

The fibers heat treated at 2700 °C in Ar, along with pristine P-100, were further examined to determine their thermal stability in air. Five of every kind of these fibers were attached to a glass slide using silver paint. These fibers were then heated to 400 °C for 10 hr, and then to 475 °C for 33 hr. Another set of slides were heated to 500 °C for 47 hr. Comparisons of the fiber diameter and electrical resistance before and after every stage of heating were used to determine the thermal stability.

Chemical Reactivity of the Fiber Products

The chemical reactions between particular metals and semiconductors and the fibers heated to 1100 °C occurred by allowing direct contact between them. The metals and semiconductors included magnesium (Mg), aluminum (Al), titanium (Ti), manganese (Mn), carbon steel, stainless steel 304, copper (Cu), zinc (Zn), silicon (Si), and lead (Pb). Reaction temperatures ranged from 800 to 1150 °C. The fibers and metals made contact in the same way as that described previously for the Pb-CF_{0.68} system.

The fiber electrical resistivity, x-ray diffraction data, scanning electron micrographs (SEM), EDS data, and weight data of the products from these reactions were measured. Some of the fiber surfaces were also characterized using ESCA analysis. Their moduli were qualitatively estimated by measuring and comparing the force needed to bend different types of fibers having the same diameter into a 5-mm-diam semicircle. In this research, the fiber diameters were in the 8- to 15-μm range.

RESULTS AND DISCUSSION

The properties of the original carbon used to fabricate CF_{0.68} and CF_{0.9} are summarized in table I and can be used for comparison with the carbon products obtained in this research. Data from the previously described experiments are summarized in tables II through X. Some important results of CF_x defluorination and their implications are shown in figure 2.

In response to the second question posed in this report's introduction, none of the fiber samples produced in this research had a diamond or diamond-like molecular structure. However, note that (1) some products obtained in this research have cross-linked graphite layers, (2) lower reaction temperature and higher reaction pressure favor the production of diamond over graphite during the process of diamond synthesis, and (3) the temperature for defluorination could be lowered if the CF_x was in a more chemically reactive environment (including ultra-violet (UV) radiation, which generates free radicals). Considering these facts, it is possible that carbon materials with a diamond or diamond-like structure could be made by exposing CF_x to more reactive chemicals (e.g., C₂H₂ or C₂HCl₃) in a UV environment with lower temperatures and higher pressures than those used here. Although beyond the scope of this study, future research will include this step.

According to EDS data, for all chemicals used here, the reaction of the CF_x fibers was slight if the temperature was too low: $<300^\circ C$ for S, $<250^\circ C$ for $BrH_2C-CH=CH-CH_2Br$, and $<350^\circ C$ for other chemicals. The CF_x samples lost a small amount of fluorine and picked up a trace amount of the chemicals that they were exposed to. At higher temperatures, however, defluorination of CF_x proceeds quickly and nearly reaches completion in 2 hr without any explosion. An explosion can occur if the defluorination is in an inert environment at a temperature above $400^\circ C$ (ref. 2).

After defluorination, the fiber products may contain fluorine up to 11 wt % carbon, and other halogens up to 31 wt % carbon, or S up to 90 wt % carbon (EDS data). The fluorine was from CF_x ; the S and other halogens, from the chemicals used in these reactions. The majority, if not all, of fluorine was removed from the chemically modified fibers by heating to $600^\circ C$ in N_2 . The majority, if not all, of other halogens (i.e., chlorine or bromine) was removed from the chemically modified fibers by heating to $1000^\circ C$ in N_2 . Some S, however, remained in the fibers after $1160^\circ C$ N_2 heating. This will be discussed later in this report.

For all products defluorinated in Br_2 , S, or halocarbon, the x-ray diffraction data showed only graphite peaks. Furthermore, EDS data obtained from the Br_2 , S, and halocarbon-defluorinated CF_x sample showed fluorine peaks much smaller than those from the N_2 - or air-defluorinated CF_x sample. This suggests that the chemicals used in this research actively remove fluorine from the carbon structure during defluorination.

The important results observed from the reactions between CF_x and the specific chemicals described are discussed in the following sections.

Nitrogen

A 0.1-g sample of $CF_{0.68}$ fibers was heated rapidly by placing it directly into $450^\circ C$ N_2 from ambient air. The resulting explosion, a bright white light and a black cloud of carbon particles, was observed through the quartz tube that contained the fibers. This observation agrees with a previous report indicating that rapid heating of CF_x at temperatures above $400^\circ C$ results in an explosion (ref. 2).

When $CF_{0.68}$ fibers made from P-100 were heated slowly in N_2 from 400 to $460^\circ C$ in 16 hr, the fibers lost weight without exploding. Subsequent heating to $1100^\circ C$ in N_2 produced carbon fibers that retained 70 percent of the original P-100 weight. The x-ray diffraction data indicated that the carbon fiber product was structurally damaged graphite.

The $CF_{0.68}$ fibers lost 6 and 50 percent of their fluorine after heating for 16.5 hr at $350^\circ C$ and 5 hr at $400^\circ C$ in N_2 , respectively.

Heating to $400^\circ C$ in N_2 for 3 hr did not cause the gray $CF_{0.9}$ fibers (from P-25) to turn black, indicating no significant fluorine loss. After 8.5 hr of heating at $400^\circ C$ in N_2 , the temperature increasing slowly from 400 to $460^\circ C$, the fiber explosion was avoided because of the slow heating rate, and the fibers turned black. Further heating to $1100^\circ C$ resulted in a carbon product that had only 42 percent of the original P-25 weight. That is, 58 percent of the carbon atoms were lost during defluorination of the $CF_{0.9}$ (from P-25) in N_2 . This result suggests that a large number of active sites are present in the remaining carbon material.

The physical properties of the fibers obtained by heating CF_x in N_2 are summarized in table II.

Air

A $\text{CF}_{0.68}$ fiber lost 7.5 percent of its weight after heating in air at 350 °C for 19 hr. At this temperature for 323 hr, however, the fiber lost 45 percent of its weight. This result suggests that an oxygen- CF_x reaction is slow but steady at 350 °C, whereas, at 400 °C in air, the fiber's loss of mass quickly reaches a level higher than the total fluorine mass in the original $\text{CF}_{0.68}$ fibers (table III). EDS data indicated that there was some remaining fluorine (about 3 wt % carbon), but very little oxygen, in the defluorinated product. This suggests that at 400 °C, oxygen attacks the carbon structure and removes carbon atoms from the CF_x in the defluorination process. Reference 1 provides additional data about the thermal stability of CF_x fibers in air.

Tin and Lead

The CF_x -Sn and/or -Pb reactions resulted in graphite fibers with tin and/or lead fluoride particles on the fiber surfaces. The EDS data, taken from even the clean area of the fibers, shows a large Pb peak (fig. 3) which indicates that the entire fiber surface is covered by some unidentified lead compound. However, x-ray diffraction data show only a graphite peak. A molecular structure similar to that of SiC was not obtained.

Bromine

The defluorination of $\text{CF}_{0.65}$ in 350 °C Br_2 vapor was near completion in 6 hr, but the $\text{CF}_{0.68}$ did not defluorinate at 350 °C in Br_2 . These results signify that different CF_x samples have different stability which depends, among other factors, on the fluorine content and the structural damage of the CF_x .

After defluorination of $\text{CF}_{0.68}$ at 450 °C in Br_2 vapor, the fibers became very fragile, indicating extensive structural damage. After heating these defluorinated fibers in N_2 at 660 °C, and then at 1100 °C, they became less fragile. Figure 4 shows the EDS data of these fibers right after defluorination and right after each of the two stages of heating. Table IV describes the properties of these fibers. The approximate bromine and fluorine content of these products can be estimated by comparing these EDS data with the reference EDS data taken from brominated P-100, which contains 18 wt % Br_2 , and from the $\text{CF}_{0.68}$, respectively.

Knowing that the fibers heated to 660 °C are essentially carbon fibers with a damaged graphite structure, and knowing that an unusually high fraction (20 percent) of the fiber mass evaporated in 1100 °C N_2 for 1 hr (table IV), reference 5 notes that C_{60} can similarly be produced by treating damaged graphite (damaged and evaporated by laser) at 1200 °C. Although not positively proven, the hypothesis in this case is that some of the 20 percent mass lost during the 1 hr of 1100 °C heating is C_{60} . If this is true, then this defluorination process could be a new way to mass-produce C_{60} .

One reason for the extensive structural damage in the CF_x fibers defluorinated in Br_2 is that Br_2 is not an effective chemical to heal the carbon structural damage during defluorination. A bromine atom is large and can only form one bond to a carbon atom. It is, therefore, difficult to fit into a structure of carbon atoms, each of which is small and can form four chemical bonds. As an attempt to heal the structural damage, the fibers were soaked in CHBr_3 at room temperature for 3 hr and then at 149.5 °C for 5.5 hr. This histogram was chosen because room temperature is the lowest possible temperature that can be obtained without a more sophisticated experimental design, and 149.5 °C, the boiling point of CHBr_3 at 1 atm, is the highest possible temperature of CHBr_3 as a liquid. It was hoped that liquid CHBr_3 would wet the fibers and reach the defects in the carbon structure, and the carbon atom in the CHBr_3 could then heal the damaged structure.

After the soaking process described in the last paragraph, the fiber diameter increased significantly, and the graphite peak in the x-ray diffraction data became significantly higher and narrower, suggesting a more crystalline and orderly molecular structure. These results can be seen by comparing the first column of table IV and first column of table V. Furthermore, subsequent heating of the fibers that were soaked with CHBr_3 caused the x-ray diffraction peak to increase (table V), whereas subsequent heating of fibers not soaked with CHBr_3 caused the peak to decrease (table IV). These phenomena suggest that, upon heating, the graphite crystals in the fibers soaked with CHBr_3 become larger and/or more numerous, whereas the graphite crystals in the fibers not soaked with CHBr_3 disintegrate. These results indicate that CHBr_3 can heal the structural damage resulting from defluorination of CF_x .

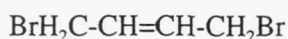
CHBr_3 , $\text{C}_2\text{H}_2\text{Br}_4$ and CCl_4

After defluorination, as described in tables VI to VIII, in CHBr_3 , $\text{C}_2\text{H}_2\text{Br}_4$, and CCl_4 vapor, respectively, and 1100°C heating to N_2 , the $\text{CF}_{0.68}$ fibers defluorinated completely without much structural damage. The fibers defluorinated in CCl_4 have a much higher and narrower graphite peak in the x-ray diffraction data (table VIII), which suggests a more orderly structure than the other two kinds of fibers. A possible explanation is that CCl_4 , because of its shorter chain length than $\text{C}_2\text{H}_2\text{Br}_4$ and its lower chemical reactivity than CHBr_3 , does not produce cross-linking between either adjacent graphite layers or adjacent graphite crystallites.

Table VII also shows that the physical properties of the fibers heat treated at 2700°C in Ar are very similar to the P-100 heat treated at 2700°C in Ar described in table I. However, these two 2700°C heat-treated fibers differ significantly in stability at 500°C in air. The difference in thermal stability was concluded by comparing diameters and electrical properties of the fibers in tables I and VII, both types air-treated for 47 hr at 500°C . The fibers defluorinated in $\text{C}_2\text{H}_2\text{Br}_4$ and heat-treated at 2700°C are less stable than the P-100 fibers heat-treated at the same temperature. This difference in thermal stability may be a result of the presence of active sites and cross-linking between graphite layers or crystallites for the $\text{C}_2\text{H}_2\text{Br}_4$ -defluorinated fibers.

$\text{CF}_{0.9}$ fibers made from P-25 exploded when they were rapidly heated to 400°C in $\text{C}_2\text{H}_2\text{Br}_4$. However, they were defluorinated by soaking in room temperature $\text{C}_2\text{H}_2\text{Br}_4$ for 7 days and then heating in $\text{C}_2\text{H}_2\text{Br}_4$ at 390°C for 3 hr. This defluorinated product is described in table VII. The resulted fibers contained a large quantity of bromine and fluorine. By EDS examination, the empirical formula for the defluorinated fibers was approximately $\text{CF}_{0.3}\text{Br}_{0.1}$. Subsequent heating to 1150°C in N_2 resulted in carbon fibers that contained little, if any, bromine or fluorine. X-ray diffraction data do not show a clear graphite peak, indicating that these fibers contain little, if any, graphite crystals. When bent and visually inspected, these fibers appeared to be soft. Whether they can be used as gasket material remains to be studied. The mass of the final carbon product was 134 percent of the initial P-25 carbon fiber mass; this suggests that the carbon in $\text{C}_2\text{H}_2\text{Br}_4$ actually became part of the final carbon fiber product (fig. 5).

When the $\text{C}_2\text{H}_2\text{Br}_4$ environment described in the preceding example was replaced by inert N_2 , results were very different. As stated previously in this report, 3 hr of heating to 400°C in N_2 did not cause significant fluorine loss. In addition, heating to 1100°C resulted in a carbon product that had only 42 percent of the original P-25 weight (table II). Comparing this with the 134 percent described in the last paragraph, the function of $\text{C}_2\text{H}_2\text{Br}_4$ to prevent or heal the damage of the CF_x carbon structure during defluorination is apparent.



At a temperature as low as 250°C , $\text{BrH}_2\text{C}-\text{CH}=\text{CH}-\text{CH}_2\text{Br}$ reacted with $\text{CF}_{0.68}$ fibers. Under this condition, two-thirds of the fluorine in the CF_x was lost in 3 hr. The same CF_x does not lose fluorine at 250°C in air or at 250°C in N_2 . These data indicate that $\text{BrH}_2\text{C}-\text{CH}=\text{CH}-\text{CH}_2\text{Br}$ reacts to carbon and drives fluorine out of CF_x .

The data suggest that, when driving out two fluorine atoms attached to the adjacent carbon layers, the ends of the $\text{BrH}_2\text{C}-\text{CH}=\text{CH}-\text{CH}_2\text{Br}$ molecules may be attached to these two adjacent carbon layers, resulting in cross-linked graphite.

Figure 6 shows a series of x-ray diffraction data at different stages of the fluorination process for P-100 fibers, defluorination by $\text{BrH}_2\text{C}-\text{CH}=\text{CH}-\text{CH}_2\text{Br}$ at 375 °C for 3 hr, and subsequent high temperature heating to 2700 °C. Physical properties of these fibers are described in table IX.

Compared with the diffraction data for the original reactant (P-100 fibers) post-heated to 2700 °C (table I), the final product of this process has a graphite peak slightly narrower and closer to the pure graphite value (3.35 Å). Furthermore, its diameter is a little larger than, and its density and electrical resistivity is about the same as, the 2700 °C post-heated P-100. This product's thermal stability in air at 500 °C, however, is much lower. In addition, its modulus is much higher than both the pristine and the 2700 °C post-heated P-100. In fact, by measuring the force needed to bend fibers and comparing it with a 5-mm semicircle, this fiber has a higher modulus than a P-120 fiber with a modulus of 120 Msi. It is suspected that this fiber's modulus is similar to that of a P-140 fiber with a modulus of 140 Msi. However, the comparison could not be made because the P-140 fibers broke before they could be bent to 5-mm semicircles.

These data suggest the hypothesis that during the defluorination reactions, the carbon chains of the $\text{BrH}_2\text{C}-\text{CH}=\text{CH}-\text{CH}_2\text{Br}$ molecules may act as bridges to cross-link the carbon atoms at defect sites, at adjacent crystallite boundaries, or at the adjacent molecular layers of the CF_x . Such carbon chain bridges prevent fiber bending, and therefore, result in high-modulus fibers. These bridges are unstable at 500 °C in air and become active sites when exposed to this condition. If the hypothesis is true, then the thermal conductivity of these chemically modified fibers could also be extremely high. Further study on this subject is needed to verify this.

After heating the fibers defluorinated in $\text{BrH}_2\text{C}-\text{CH}=\text{CH}-\text{CH}_2\text{Br}$ to 1100 °C, the fiber product is composed of pure carbon and has an unusually large diameter (12.5 μm; see table IX). This again can be explained with the cross-linking between carbon atoms by the long $\text{BrH}_2\text{C}-\text{CH}=\text{CH}-\text{CH}_2\text{Br}$ chain. The chain pushes the carbon structure and/or graphite crystallites apart and, therefore, causes the fiber diameter to increase.

Sulfur

$\text{CF}_{0.9}$ fibers (from P-25) reacted very slowly, if at all, to a 1-atm, air-saturated sulfur-vapor mixture at 315 °C. However, the reaction to this vapor mixture at 370 °C was near completion in 10 hr. Table X summarizes the product of this defluorination. Immediately after the defluorination reaction, the sulfur-to-carbon ratio in most fibers was estimated to be about 1:9. However, in some fibers, the value was as high as 1:1 to 3 (EDS data) based on $[\text{Si}(\text{CH}_3)_2\text{O}]_n$ and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ as EDS reference materials for the estimation of the oxygen-to-carbon ratio and the sulfur-to-oxygen ratio, respectively. After heating to 660 °C in N_2 , the sulfur-to-carbon atomic ratio for the defluorinated fibers was more uniform and was estimated by EDS to be about 1:10, but weight measurement indicated that the final product was 107 percent of the original P-25 weight. Similar to the $\text{C}_2\text{H}_2\text{Br}_4$ defluorination of $\text{CF}_{0.9}$, the fibers appeared to be soft and could possibly be used as a high-temperature gasket material.

A commercially purchased $\text{CF}_{0.9}$ powder sample defluorinated at 370 °C in S in the same way as the other CF_x fibers. This suggests that all graphite fluorides, regardless of their geometric shapes, will defluorinate similarly.

A PTFE sample was also tested at 370 °C in S. No reaction could be detected.

Sulfur starts to react quickly with $\text{CF}_{0.68}$ fibers (from P-100) at 300 °C. This is lower than the temperature (>350 °C) at which decomposition of the $\text{CF}_{0.68}$ fibers in N_2 is noticeable. This is also lower than the temperature (>315 °C) at which $\text{CF}_{0.9}$ (from P-25) begins to react with S noticeably.

After defluorination of the $\text{CF}_{0.68}$ fibers (from P-100) in S heated to 370 °C for 10 hr and subsequent heating in N_2 to 1100 °C, the sulfur-to-carbon ratio in the fibers is estimated to be typically 1:10 to 30 (table X). ESCA analysis indicates that the sulfur-to-carbon ratio on the surface of these fibers was 1:25 and 1:175 when the fibers were just defluorinated and just heated to 1100 °C in N_2 , respectively.

In this research, S is the only chemical which remains in a large quantity in carbon fibers heat treated at 1100 °C. The x-ray diffraction data of these C_{10-30}S fibers described in the last paragraph showed only graphite peaks. These peaks are the most narrow for all the samples heated to 1100 °C. Also, these fibers have the lowest resistivity value of all the samples heated to 1100 °C (tables II and IV through X). The results suggest that sulfur-containing fibers heated to 1100 °C are chemical compounds where S does not cross-link different graphite layers or different crystallites, but is doped into the carbon structure.

Table X also describes the properties of the carbon fibers produced by defluorination of $\text{CF}_{0.68}$ (from P-100) in S and subsequently heated in Ar to 2700 °C. These sulfur-containing fibers have properties similar to the carbon fibers that were obtained by heating P-100 (i.e., the original reactant of this complete process) to 2700 °C in Ar (table I).

Thermal Stability of Heat-Treated Fibers

Using the changes of fiber diameter and electrical resistivity caused by heating in air as the criteria, all 2700 °C heat-treated fibers were found to be stable in 400 °C air. At 475 °C in air, however, the fibers defluorinated and then heat treated at 2700 °C began to deteriorate noticeably. The P-100 fibers heat treated at 2700 °C are stable in air until the temperature reaches 500 °C. Among the defluorinated and then 2700 °C heat-treated fibers, the air thermal stability depends on the environment in which the fibers are defluorinated. The air thermal stability increases if the fibers were defluorinated in $\text{BrH}_2\text{CHC}=\text{CHCH}_2\text{Br}$, S, or $\text{C}_2\text{H}_2\text{Br}_4$. This order of increasing thermal stability may result from the decreasing number of cross-links between graphite layers in these fibers.

Chemical Reactivity of Activated Graphite

Pristine P-100 and P-25 do not react with metals or semiconductors, whereas the fibers that were defluorinated and then heated to 1100 °C in N_2 (described in previous section) do react with some metals or semiconductors. These fibers are pure carbon and have the same x-ray diffraction data as graphite. However, because their chemical reactivity is closer to activated carbon than to regular graphite, they are tentatively called "activated graphite."

The chemical reactivities of activated graphite are summarized in the following paragraphs. Note that activated graphite can collect certain metals (e.g., Mn) or be intercalated with certain metals (e.g., Mg). Therefore, it can be used as a supporting material for these metals in industrial applications (e.g., in catalyst fabrication or in battery fabrication).

Strong chemical reaction.—The defluorinated fibers are scavengers for Mn at high temperatures. They removed the small amount of Mn in carbon steel when they were in direct contact with it at 1100 °C. Also, they reacted with solid Mn at 800 and 1150 °C, resulting in fibers coated with the metal (fig. 7). The x-ray diffraction data for the samples not totally coated by the metal show graphite peaks that are low and broad. In addition, in the case of a Mn-S fiber reaction at 800 °C, three new sharp peaks at 9.51, 4.78, and 3.19 Å were observed. These

could be the x-ray diffraction peaks for a new first stage intercalation compound whose I_c (identity period) value is 9.51 Å, and whose intercalate contains S and Mn.

Doping.—The defluorinated fiber-liquid Al reactions at 1100 °C resulted in a fiber product with lower electrical conductivity, a broader x-ray diffraction peak, lower modulus, but a higher strain-to-failure ratio. Although EDS data does not show an Al peak, it is possible that a small number of Al atoms did diffuse into the graphite structure and possibly became trapped at defect sites.

Intercalation.—The defluorinated fiber-liquid Mg reactions at 1050 °C resulted in a 100-percent increase in electrical resistivity in air. The x-ray diffraction data show a broader graphite peak; the EDS data, the presence of Mg and oxygen. The presence of oxygen suggests oxidation of Mg in or on the fibers. Although the higher electrical conductivity suggests intercalation, the x-ray diffraction data did not identify an obvious intercalation peak. Intercalation of Mg into the carbon material is believed to be very difficult, if possible at all, and has not been reported previously. The fact that Mg can be intercalated with this carbon product suggests that this product has a generally high reactivity in terms of intercalation.

Wetting or surface reaction.—Direct fiber-Si contact at 1100 °C resulted in fibers containing some Si (EDS data) and slightly decreased fiber mass and electrical conductivity. In addition, the x-ray diffraction peak of this carbon material became slightly broader and had a slightly higher interplanar spacing value. This material's thermal stability in air increased. All data suggest the possibility that Si reacted to the carbon fibers to form SiC on the fiber surface at 1100 °C. The SiC-coated carbon fibers can be used to fabricate a strong carbon-ceramic matrix composite.

Direct fiber-titanium (Ti) contact at 1100 °C also caused small decreases of fiber electrical conductivity and a slightly broader x-ray diffraction peak. The fibers contained a small amount of Ti. This suggests the formation of titanium carbide on or near the fiber surface.

For Ti, SS 304, carbon steel, nickel (Ni), and Cu, the fiber-metal reactions at 1100 °C caused the fibers to contain some metal, EDS data show, but did not cause observable changes in their weight, electrical resistivity, and x-ray diffraction peaks. These are believed to be simple wetting, where metal is formed only on the fiber surfaces.

The combination effect of Cu and SS 304 is an interesting observation. The fiber-SS 304 reaction and the fiber-Cu reaction were not obvious, but the fiber-copper foil-SS 304 wire mesh reaction at 1100 °C and 1 atm pressure (i.e., no external pressure) resulted in a strong composite. Figure 8 shows two composites made from, respectively, the copper foil-SS 304 wire mesh "alloy" and the fibers defluorinated in $C_2H_2Br_4$ and then heated to 1100 °C in N_2 ; and this alloy and the P-100 fibers. Most of the chemically modified fibers were wetted by the alloy without external pressure at 1150 °C, but only a small fraction of the pristine P-100 fibers were wetted by the alloy under the same conditions. Furthermore, the chemically modified fibers that appear to be nonwet actually contain a significant amount of chromium, whereas the P-100 fiber that appears nonwet contains only a little, if any, metal (EDS data, fig. 9). Therefore, the wetting between this alloy and the chemically modified fiber appears to be easier than the wetting between this alloy and the P-100 fiber.

These results suggest that the alloy made from treating copper foil and SS 304 wire mesh at 1150 °C in N_2 could be a high temperature adhesive for carbon-carbon composites. In the experiments conducted herein, this alloy was so strongly adhered to the pyrolytic graphite sample holder that an attempt to separate them resulted in a break in either the alloy or the pyrolytic graphite, but not in their interface.

No reactions.—No fiber-zinc reactions were observed; that is, the fiber properties were unchanged. Figure 10 summarizes some of the results of the fiber-metal reactions.

To obtain data on chemical reactivities of activated graphite, the fibers studied were from defluorination of $CF_{0.68}$ samples in a chemically reactive, vaporous environment. If the defluorination of the same fibers was conducted in an inert environment, the resulting activated graphite would have a large number of active sites and, therefore, have different chemical reactivities. The chemical reactivities of the activated graphite fibers obtained in N_2 environments will be described in a separate report (ref. 6).

CONCLUSIONS

The study described herein demonstrated that carbon materials with desirable properties can be produced by causing different materials to react with CF_x at various temperatures and pressures. Graphite fluoride can be made easily by fluorination of pitch-based carbon fibers.

The materials developed in these experiments include those which have known useful properties and those which could possibly be useful. The former includes very high modulus carbon fibers that may also be highly thermally conductive, and fibers that can form metal matrix composites more easily than the pristine carbon fibers can. The latter includes CS_x fibers ($0 \leq x \leq 1$) made from P-25, which are apparently soft and could be used as a high temperature gasket material.

Making C_{60} according to the process described in this report is not yet conclusive. However, knowing from previous research that the carbon mass C_{60} evaporated at 1200 °C from a structurally damaged graphite sample, it is possible that the carbon mass evaporated at 1120 °C from a structurally damaged graphite sample in this research is also a fullerene. The difference between previous and present research is that the former graphite structural damage was caused by laser irradiation, but the later graphite structural damage was caused by reactions to F_2 .

Making diamond or diamond-like fibers according to this process was not successful.

A process developed in this work is to use $CHBr_3$ in particular, or perhaps some other organic halocarbon in general, to heal the defects of the graphite structure.

A "by-product" of this work is an alloy obtained by treating copper foil and SS 304 wire mesh together at 1150 °C. This melt can form metal matrix composites with all carbon materials studied in this lab (including P-100 fibers), and can be an effective adhesive for carbon-carbon composites.

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TABLE I.—PHYSICAL PROPERTIES OF COMMERCIALY PURCHASED CARBON FIBERS

Property	P-100		Heat-treated P-100 ^a		P-25	Heat-treated P-25 ^a
	No post-heating	500 °C for 47 hr in air	No post-heating	500 °C for 47 hr in air		
Diameter, μm	10.0	(b)	10.2	9.1	10.8	10.0
Resistivity, $\mu\Omega\text{-cm}$	390		310	360	1500	380
Resistance, $\Omega\text{/cm}$	510		410	550	1670	490
X-ray diffraction						
Peak position, \AA	3.375		^c 3.362, 3.367	---	3.37 to 3.52	3.375
Peak width at half max position, deg	0.454		^c 0.343, 0.397	---	2.6	0.450
Weight ratio to original carbon	1.0		0.80	---	1.0	0.71
Density	2.18		2.16	---	-----	----

^aHigh-temperature heat-treated first at 2700 °C in Ar.^bFibers broke into pieces.^cMeasured twice.TABLE II.—PHYSICAL PROPERTIES OF CARBON MATERIALS OBTAINED
FROM HEAT TREATING CF_x IN N_2

Property	$\text{CF}_{0.68}$ (from P-100)			$\text{CF}_{0.9}$ (from P-25)
	400 °C for 5 hr	Sequence A (a)	Sequence B (b)	400 to 460 °C for 8.5 hr, then 1100 °C
Diameter, μm	-----	10.5	9.7	-----
Electrical resistivity, $\mu\text{m-cm}$	-----	3740	1900	-----
X-ray diffraction				
Peak position, \AA	3.48	3.39	3.4	3.38
Peak width at half max position, deg	2.5	1.61	1.81	^c \approx 3.5
Weight ratio to original carbon	^d 1.54	0.74	0.70	0.42

^aHeated to 365 ° for 7 hr 460 ° for 8 hr, and then 460 to 650 ° for 7 hr.^bSequence A, and then 1100 °C for 1 hr.^cPeak height very low.^dIncomplete defluorination.TABLE III.—X-RAY DIFFRACTION AND WEIGHT DATA OF CARBON MATERIALS OBTAINED
FROM HEAT TREATING $\text{CF}_{0.68}$ IN AIR TO 400 °C FOR 4 HR

X-ray diffraction	
Peak position, \AA	3.37
Peak width at half max position, deg	2.1
Weight ratio to original carbon	0.83

TABLE IV.—PHYSICAL PROPERTIES OF CARBON MATERIALS OBTAINED
FROM HEAT TREATING $\text{CF}_{0.68}$ IN Br_2

[At room temperature for 17.5 hr, and then heated to 450 °C for 2.3 hr, followed by high-temperature treatments in N_2 .]

Property	After defluorination	After heating to 660 °C in N_2	After heating to 1120 °C in N_2
Diameter, μm	10.6	9.5	10.1
Resistivity, $\mu\Omega\text{-cm}$	2930	1500	1250
Resistance, Ω/cm	3190	2150	1560
X-ray diffraction			
Peak position, Å	3.42	-----	3.35
Peak width at half max position, deg	1.7	-----	1.6
Relative peak height	(a)	-----	(a)
Weight ratio to original carbon	1.09	0.90	0.73

^aX-ray diffraction peak decreased with subsequent heating in N_2 to 1100 °C.

TABLE V.—PHYSICAL PROPERTIES OF CARBON MATERIALS OBTAINED FROM
HEAT TREATING Br_2 -DEFLUORINATED $\text{CF}_{0.68}$
(DESCRIBED IN TABLE IV) IN CHBr_3

[At room temperature for 3 hr, then heated to 149.5 °C for 5.5 hr, followed by high-temperature treatments in N_2 .]

Property	After CHBr_3 treatment	After heating to 660 °C in N_2	After heating to 1120 °C in N_2
Diameter, μm	12.4	9.9	10.3
Resistivity, $\mu\Omega\text{-cm}$	4850	1750	990
Resistance, Ω/cm	4020	2270	1200
X-ray diffraction			
Peak position, Å	3.43	-----	3.35
Peak width at half max position, deg	1.0	-----	1.5
Relative peak height	(a)	-----	(a)
Weight ratio to original carbon	1.12	0.73	0.68

^aX-ray diffraction peak increased after soaking in liquid CHBr_3 . Further height increase was observed with subsequent heating to 1100 °C in N_2 .

TABLE VI.—PHYSICAL PROPERTIES OF CARBON MATERIALS OBTAINED FROM
HEAT TREATING $\text{CF}_{0.68}$ IN CHBr_3

[At room temperature for 65 hr, then heated to 450 °C for 1.5 hr, followed by
high-temperature treatments in N_2 .]

Property	After defluorination	After heating to 660 °C in N_2	After heating to 1120 °C in N_2
Diameter, μm	12.0	----	11.3
Resistivity, $\mu\Omega\text{-cm}$	1410	----	900
Resistance, Ω/cm	1270	----	900
X-ray diffraction			
Peak position, Å	3.38	----	3.35
Peak width at half max position, deg	1.7	----	1.4
Weight ratio to original carbon	^a 1.25	1.07	0.97

^aHigh bromine concentration in fibers.

TABLE VII.—PHYSICAL PROPERTIES OF CARBON MATERIALS OBTAINED FROM HEAT TREATING CF_x IN $\text{C}_2\text{H}_2\text{Br}_4$
AND FOLLOWED BY HIGH TEMPERATURE TREATMENTS IN N_2

Property	$\text{CF}_{0.68}$ from P-100 in $\text{C}_2\text{H}_2\text{Br}_4$						$\text{CF}_{0.9}$ from P-25 in $\text{C}_2\text{H}_2\text{Br}_4$ at room temperature for 7 days, then 390 °C for 3 hr	
	300 to 400 °C for 40 min, then 425 to 465 °C for 40 min		Room temperature for 4 days, then 400 °C for 4 hr					
	No post- heating	1100 °C in N_2	No post- heating	1100 °C in N_2	2700 °C in Ar	2700 °C in Ar, then 500 °C in air for 47 hr	No post- heating	1150 °C in N_2
Diameter, μm	12.4	11.2	----	9.9	9.8	8.6	-----	-----
Resistivity, $\mu\Omega\text{-cm}$	1530	870	----	1480	310	410	-----	-----
Resistance, Ω/cm	1288	900	----	1850	420	710	-----	-----
X-ray diffraction								
Peak position, Å	3.40	3.37	----	3.35	3.367	-----	≈3.6	≈3.6
Peak width at half max position, deg	1.8	0.81	----	1.32	0.380	-----	≈7	≈5
Weight ratio to original carbon	1.28	0.94	1.05	0.88	0.78	-----	2.64	1.34
Empirical formula	$\text{CB}_{0.027}\text{F}_{0.025}$	-----	----	-----	-----	-----	$\text{CF}_{0.3}\text{Br}_{0.1}$	

TABLE VIII.—PHYSICAL PROPERTIES OF CARBON MATERIALS OBTAINED FROM
HEAT TREATING $\text{CF}_{0.68}$ IN CCl_4

[At room temperature for 5 days, then heated to 450 °C for 8.7 hr, followed by
high-temperature treatments in N_2 .]

Property	After defluorination	After heating to 660 °C in N_2	After heating to 1120 °C in N_2
Diameter, μm	9.5	----	9.5
Resistivity, $\mu\Omega\text{-cm}$	1540	----	930
Resistance, Ω/cm	2180	----	1360
X-ray diffraction			
Peak position, Å	3.42	----	3.36
Peak width at half max position, deg	1.3	----	0.62
Relative peak height	(a)	----	-----
Weight ratio to original carbon	0.92	0.90	0.83

^aX-ray diffraction peak is higher than those obtained by defluorination in either CHBr_3 or $\text{C}_2\text{H}_2\text{Br}_4$.

TABLE IX.—PHYSICAL PROPERTIES OF CARBON MATERIALS OBTAINED FROM HEAT TREATING $\text{CF}_{0.68}$
IN $\text{BrH}_2\text{C-CH=CH-CH}_2\text{Br}$

[At 50 °C for 3 days, and then heated to 370 °C for 3 hr, followed by high-temperature treatments in N_2 and Ar.]

Property	After defluorination	After heating to 1100 °C in N_2	After heating to 2700 °C in Ar	After heating to 2700 °C in Ar, then to 500 °C in air for 47 hr
Diameter, μm	13.4	12.5	10.7	9.6
Resistivity, $\mu\Omega\text{-cm}$	1950	1020	310	600
Resistance, Ω/cm	1440	830	340	740
X-ray diffraction				
Peak position, Å	3.41 to 3.50	3.35 to 3.38	^a 3.360, 3.367	-----
Peak width at half max position, deg	2.0	1.0	^a 0.334, 0.343	-----
Weight ratio to original carbon	1.42	^b 0.97	0.70	-----
Empirical formula	$\approx\text{CF}_{0.07}\text{Br}_{0.08}$	C	C	C
Density	-----	-----	2.12	-----

^aMeasured twice.

^bNo observable halogen.

TABLE X.—PHYSICAL PROPERTIES OF CARBON MATERIALS OBTAINED FROM HEAT TREATING CF_x IN S
FOLLOWED BY HIGH-TEMPERATURE TREATMENTS

Property	$\text{CF}_{0.68}$ (from P-100) heated to 230 °C in S for 20 hr, then to 360 °C for 5 hr			$\text{CF}_{0.9}$ (from P-25) heated to 370 °C in S for 10 hr	
	No post- heating	1100 °C in N_2	2700 °C in Ar	No post- heating	650 °C for 0.5 hr
Diameter, μm	10.4	10.6	10.1	-----	16.4
Resistivity, $\mu\Omega\text{-cm}$	10.0	810	300	-----	8810
Resistance, Ω/cm	1230	940	400	-----	3370
X-ray diffraction					
Peak position, Å	3.44	3.39	3.364	3.50	3.45
Peak width at half max position, deg	1.4	0.52	0.397	≈ 8	≈ 7
Weight ratio to original carbon	1.04	0.92	0.84	1.51	1.07
Empirical formula	-----	$\text{CS}_{0.03-0.1}$	C	$\text{CS}_{0.1}$	-----

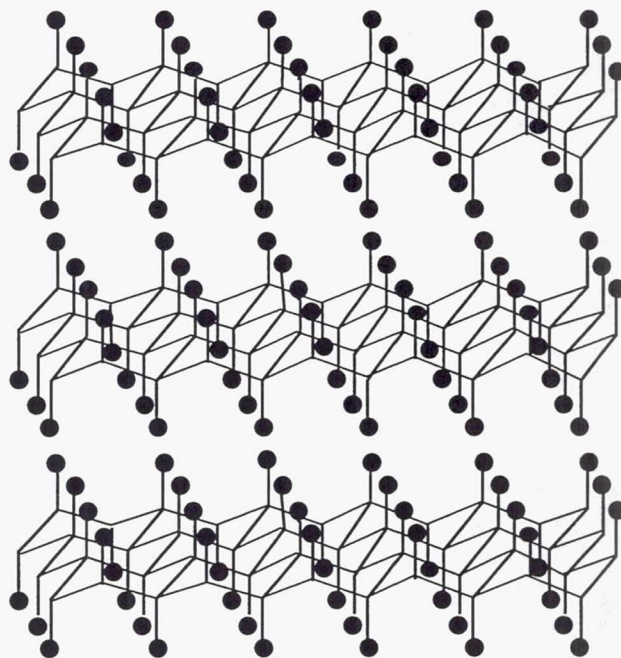


Figure 1.—Molecular structure of graphite fluoride.

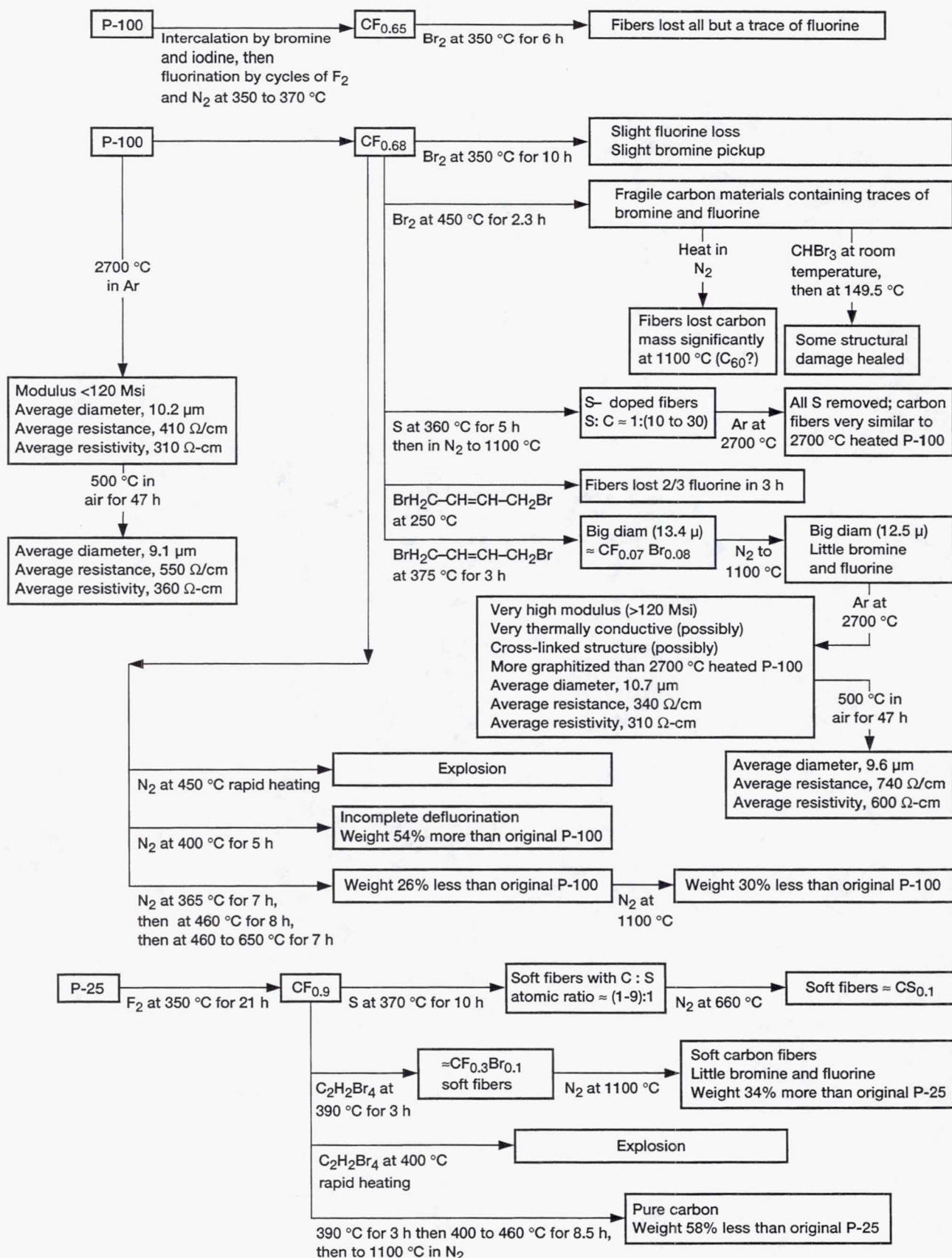


Figure 2.—Defluorination experiments conducted in this study.

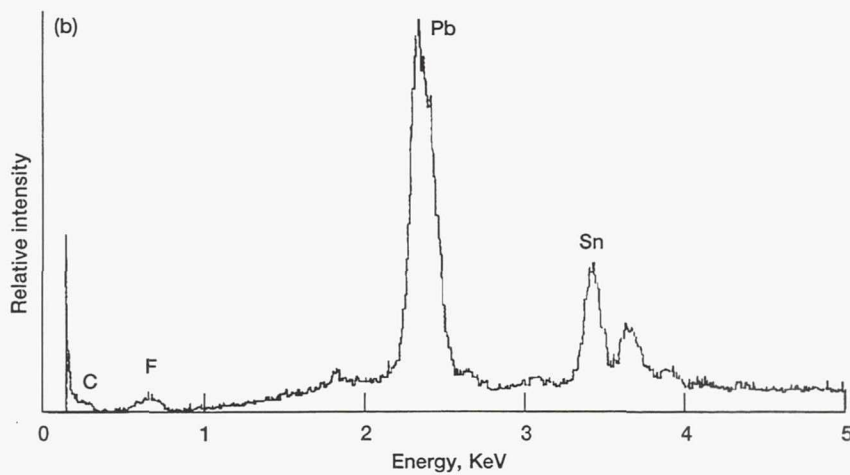
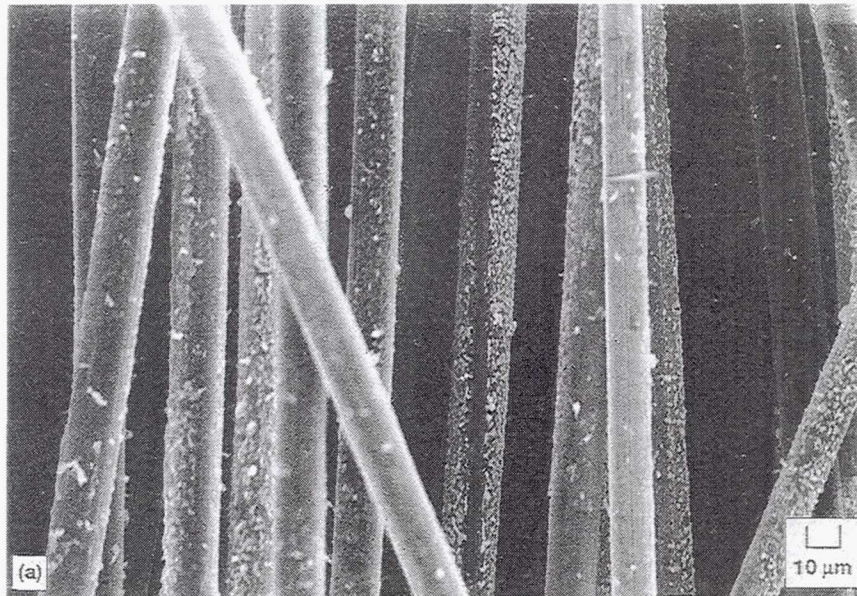


Figure 3.—CF_x fibers exposed to solder (tin-lead mixture) at 400 °C. (a) SEM micrograph. (b) EDS data obtained from clean area of fibers.

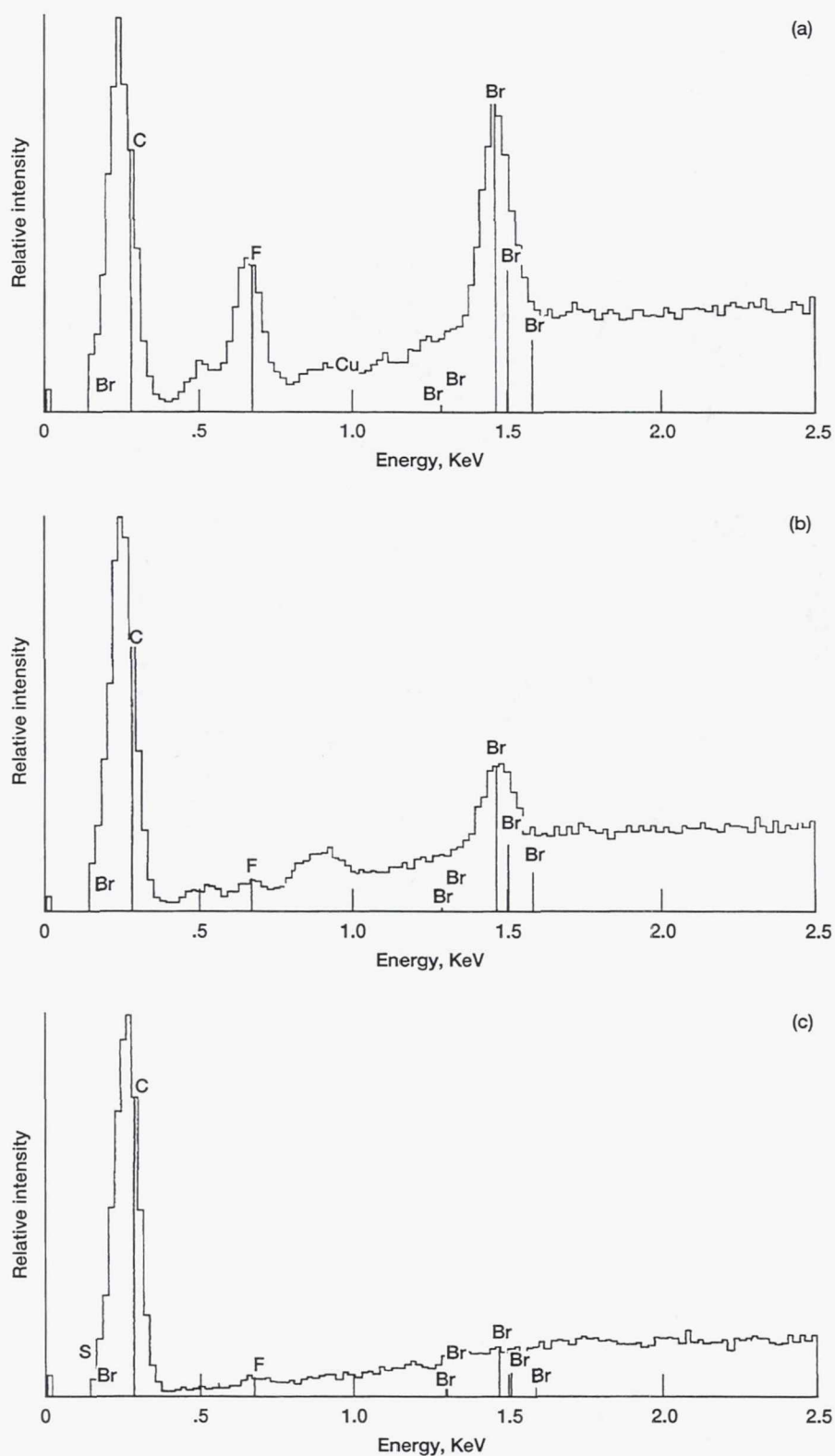


Figure 4.—EDS data for defluorinated CF_{0.68} fibers. (a) After 450 °C Br₂ treatment. (b) After 450 °C Br₂ treatment and 660 °C N₂ treatment. (c) After 450 °C Br₂ treatment, 660 °C N₂ treatment, and 1100 °C N₂ treatment.

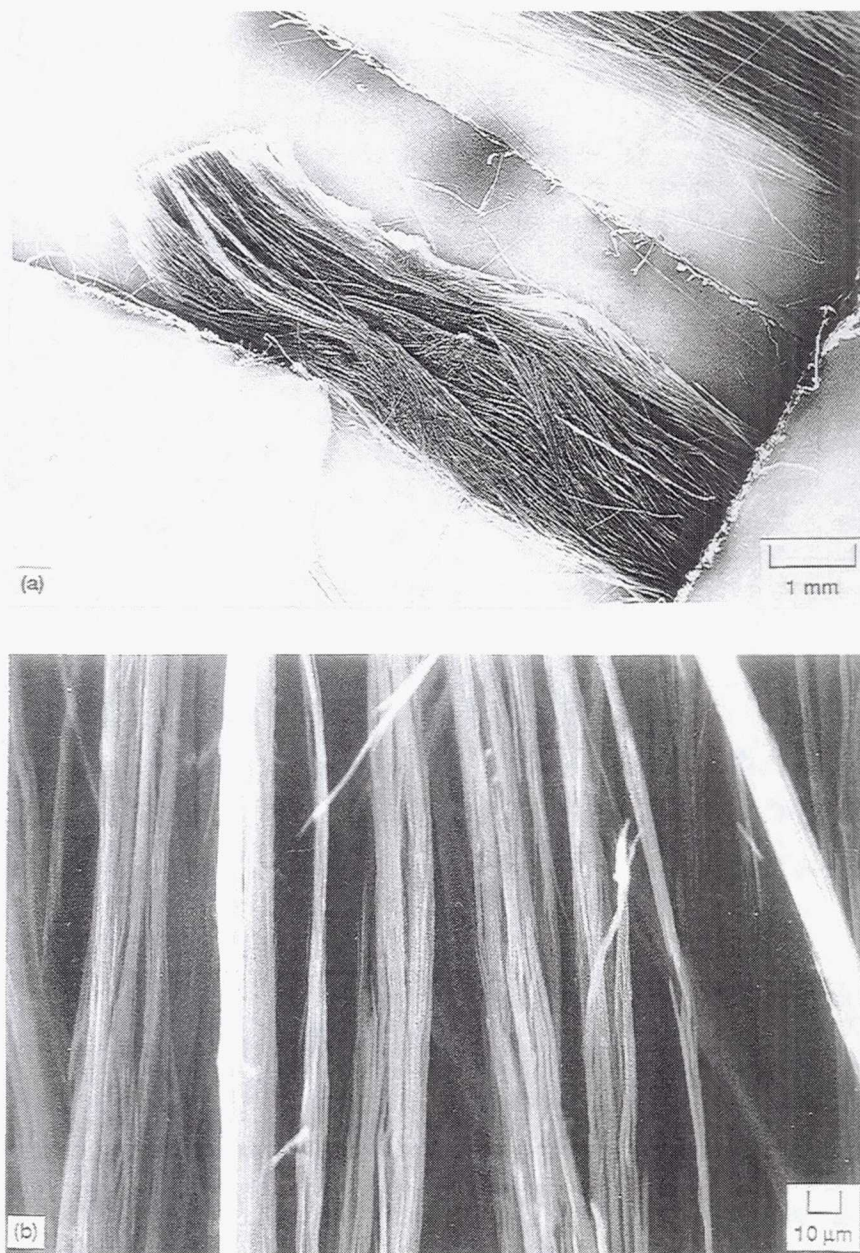


Figure 5.—Carbon fibers from defluorinated $\text{CF}_{0.9}$ (from P-25). (a) Heated to 400 °C in $\text{C}_2\text{H}_2\text{Br}_4$ for 3 h. (b) Then heated to 1100 °C in N_2 .

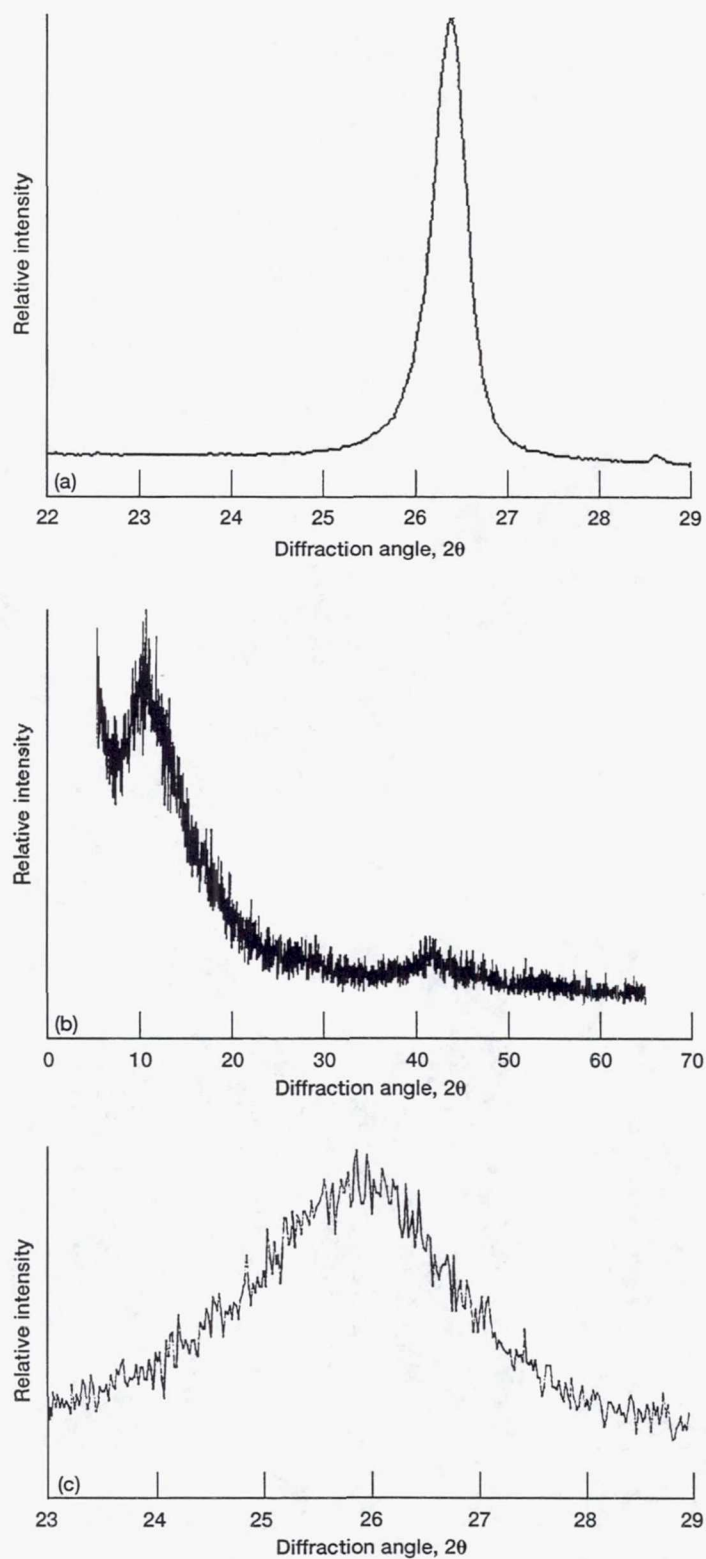


Figure 6.—X-ray diffraction data for sample before and after fluorination, defluorination, and high temperature treatment. (a) Pristine P-100 fibers. (b) CF_{0.68} after fluorination. (c) After defluorination in BrH₂CCH=CHCH₂Br at 370 °C for 3 h.

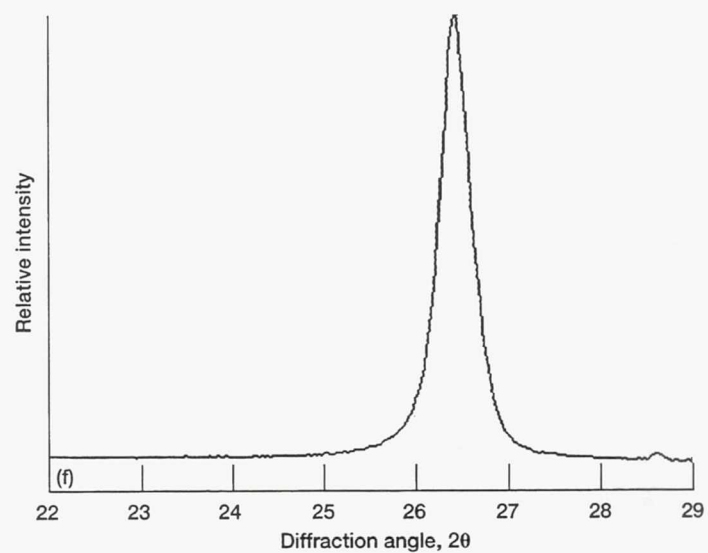
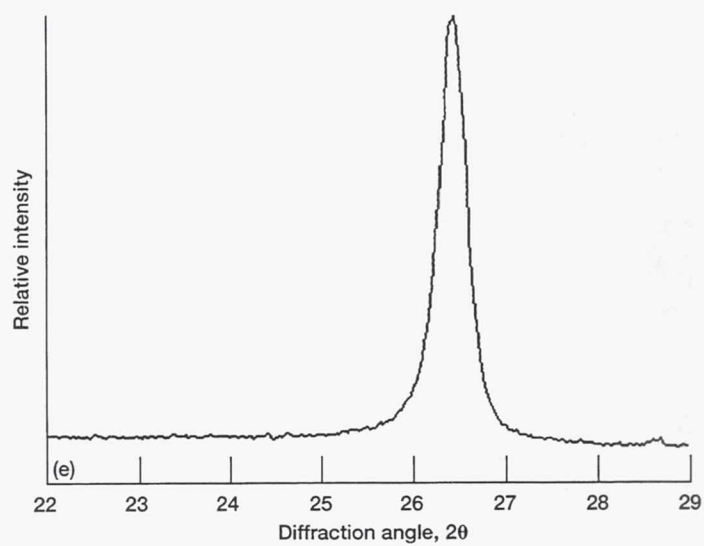
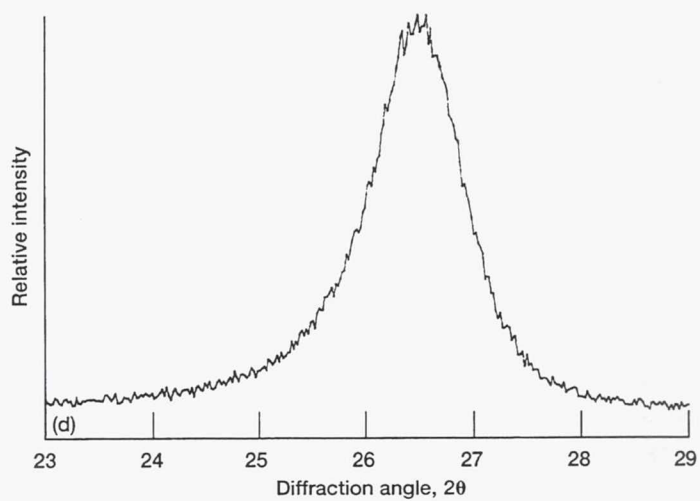


Figure 6.—Concluded. (d) After heating to 1100°C in N_2 . (e) After heating to 2700°C in Ar. (f) P-100 heat-treated at 2700°C .

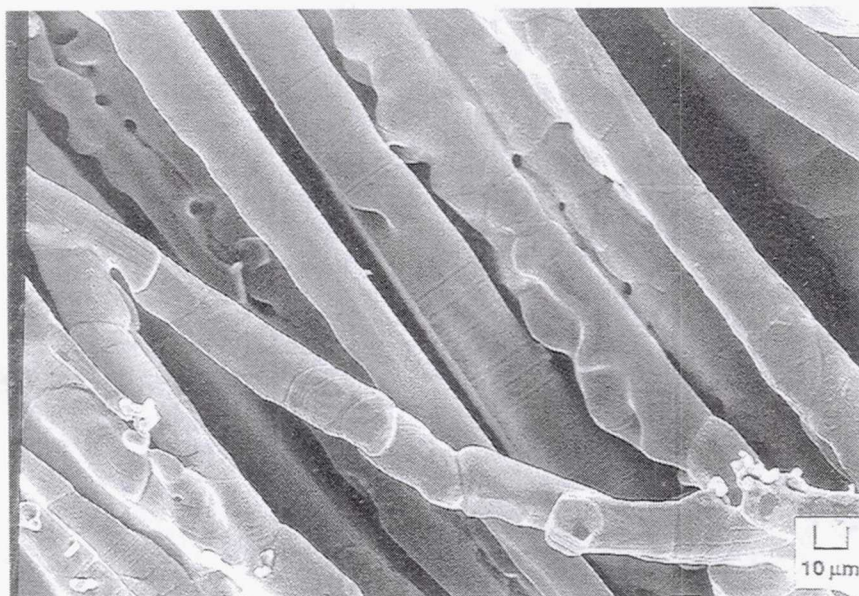


Figure 7.—Mn-coated graphite fibers from direct contact of activated graphite with solid Mn at 1100 °C in N₂.

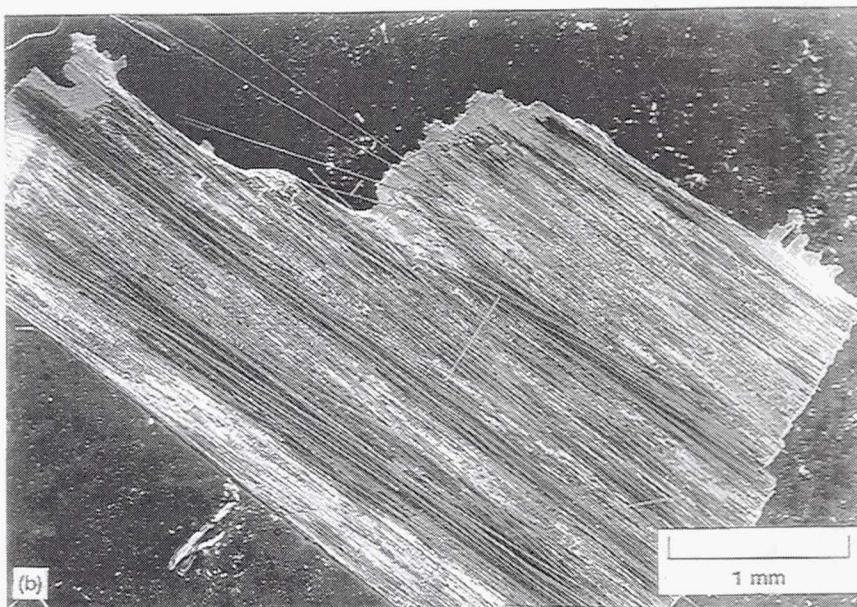
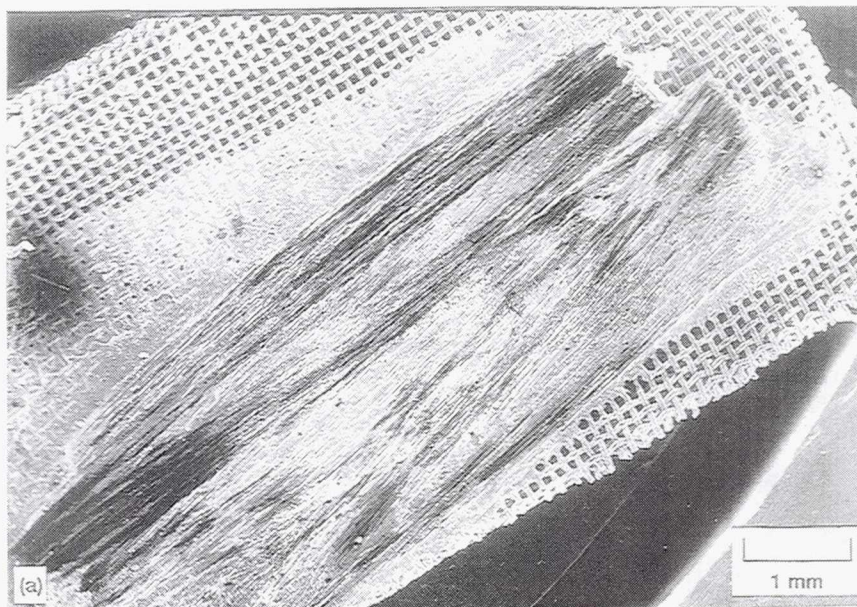


Figure 8.—Composites made from exposing carbon fibers to copper foil and SS304 wire mesh at 1150 °C at the same time. (a) Pristine P-100. (b) Defluorinated $CF_{0.68}$ or activated graphite.

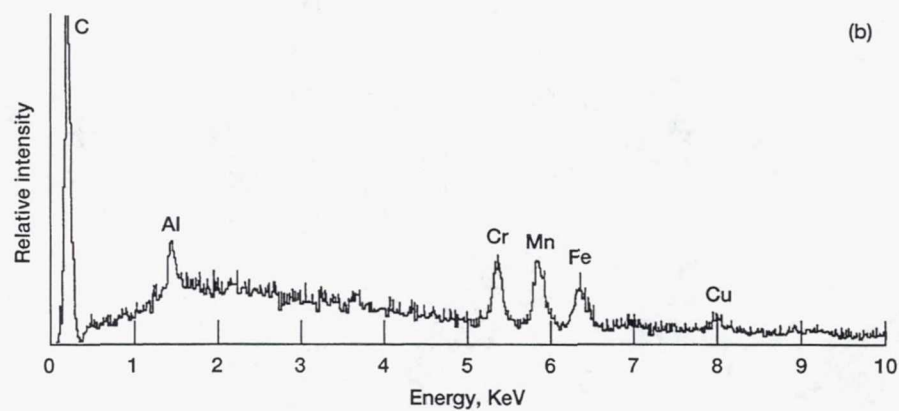
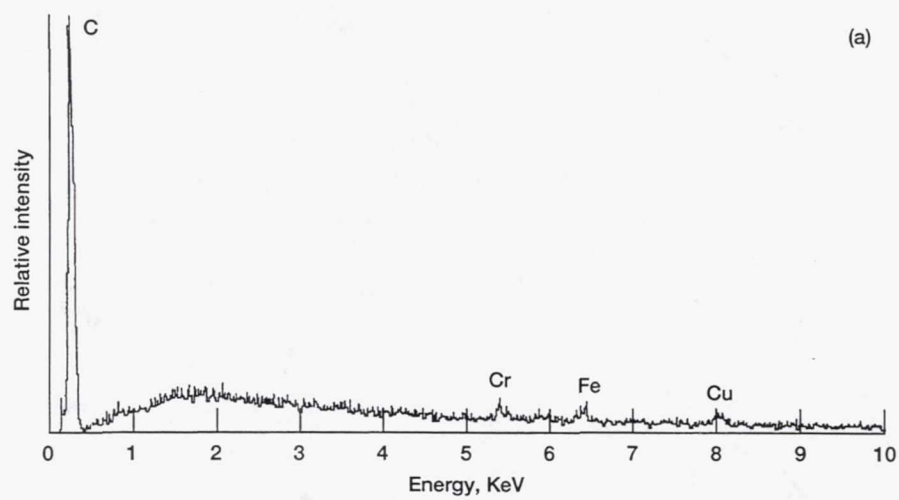


Figure 9.—EDS data for carbon fibers exposed to Cu and SS304 at the same time and appeared to be clean. (a) Pristine P-100. (b) Defluorinated CF_{0.68}.

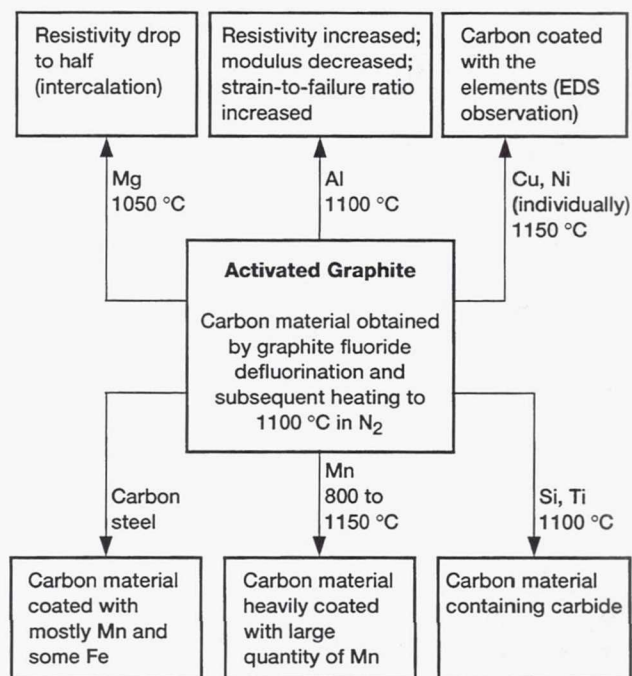


Figure 10.—Chemical reactivities of defluorination $CF_{0.68}$, or activated graphite.

REPORT DOCUMENTATION PAGE

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13. ABSTRACT (Maximum 200 words) Defluorination of graphite fluoride (CF_x) by heating to temperatures of 250 to 450 °C in chemically reactive environments was studied. This is a new and possibly inexpensive process to produce new carbon-based materials. For example, $CF_{0.68}$ fibers, made from P-100 carbon fibers, can be defluorinated in $BrH_2C-CH=CH-CH_2Br$ (1,4-dibromo-2-butene) heated to 370 °C, and graphitized to produced fibers with an unusually high modulus and a graphite layer structure that is healed and cross-linked. Conversely, a sulfur-doped, visibly soft carbon fiber was produced by defluorinating $CF_{0.9}$ fibers, made from P-25, in sulfur (S) vapor at 370 °C and then heating to 660 °C in nitrogen (N_2). Furthermore, defluorination of the $CF_{0.68}$ fibers in bromine (Br_2) produced fragile, structurally damaged carbon fibers. Heating these fragile fibers to 1100 °C in N_2 caused further structural damage, whereas heating to 150 °C in bromoform ($CHBr_3$) and then to 1100 °C in N_2 healed the structural defects. The defluorination product of CF_x , tentatively called activated graphite, has the composition and molecular structure of graphite, but is chemically more reactive. Activated graphite is a scavenger of manganese (Mn), and can be intercalated with magnesium (Mg). Also, it can easily collect large amounts of an alloy made from copper (Cu) and type 304 stainless steel to form a composite. Finally, there are indications that activated graphite can wet metals or ceramics, thereby forming stronger composites with them than the pristine carbon fibers can form.				
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